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NEW, HIGHLY EFFECTIVE ADDITIVES FOR REDUCTION OF THE CONGELATION POINT OF LUBRICATING OILS

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[Tables and figures referred to are appended.]

At present, automobiles are run for the most part under both winter and summer conditions using the same type of oil, "Avtol" 10, purified with sulfuric acid. Even in summer the operating qualities of this oil are unsatisfactory. Starting a cold engine on this oil in winter is very difficult because of the oil's high viscosity and low index of viscosity. Because of the high congelation temperature, the rate of oil feed to the parts of the engine exposed to friction is unsatisfactory, particularly in the period right after starting, and as a result, automobile engines wear out rapidly in winter. One of the important problems in improving the quality of oils designed for internal-combustion engines is that of lowering the congelation temperature and increasing the index of viscosity.

A partial lowering of the congelation temperature of oils can be achieved by dewaxing. However, dewaxing can not be considered a rational means for lowering the congelation temperature of a lubricating oil when this temperature must be reduced to minus 20-30° or lower. Deep dewaxing greatly reduces the yield of oil. As a result, additives have received widespread employment for reducing the congelation temperature of oils. A large number of diverse substances have been proposed for this purpose. As early as 1933, in the US, synthetic tetraalkylnaphthalene, which had been proposed by Davis (1) and introduced under the name of Paraflow, received wide application as an additive for lowering the congelation temperature of lubricating oils. In 1933, the synthesis and production of Paraflow was adopted by us in the USSR. Of the additives which have been proposed in

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the US more recently, another substance besides Paraflow which has received widespread use and is distinguished by high effectiveness was proposed in the patent of Reiff and Badertsher (2). It is known as Santopour. The production of both of these additives is based on the condensation of chlorinated paraffin with naphthalene or phenol, which is then converted into the phthalic ester.

A study of the crystallization processes of normal paraffin hydrocarbons together with isoparaffins convinced us that the process of crystal nuclei formation and their growth is retarded by the introduction into the paraffin molecule of aryl or complex aryl-containing radicals in place of one of the hydrogen atoms, destroying the elements of crystal-lattice symmetry of the aliphatic hydrocarbon. The elements of crystal-lattice symmetry of a paraffin take on a different character when highly branched hydrocarbons are added to the paraffin in place of normal hydrocarbons.

These considerations caused us to expect a large effect from depressants, which are similar to Paraflow and Santopour, and have branched rather than normal alkyl groups.

We prepared two compounds, which we called Naftezin /naphthezin/ and Ftalezin /phthalezin/. The effectiveness of these compounds was compared with that of samples of Paraflow and Santopour obtained from the US.

The additives were tested in four samples of oil, whose characteristics are shown in Table 1.

In practice, the most common additive to oil is Paraflow in a quantity of 0.5-1% of the weight of the oil; at these concentrations Paraflow is highly effective and also the most advantageous from the economic viewpoint. For Santopour the quantity added is smaller, being equal only to 0.25-0.5% of the weight of the oil. We used concentrations of Naftezin and Ftalezin identical to the concentrations of Paraflow and Santopour.

Table 2 shows the congelation temperatures of oils containing the additives Paraflow and Naftezin. In all cases Naftezin was a more effective additive than Paraflow. A depression of 30° in the congelation temperature of Avtol 10 purified with sulfuric acid was achieved by the addition of 1% Naftezin, while no such results could be obtained with any quantity of Paraflow.

Table 3 shows the congelation temperatures of oils containing admixtures of Santopour and Ftalezin. For all the oils which we tested, Ftalezin was a more effective additive than Santopour, and it is the most highly effective additive for the depression of the congelation temperature which has been known up to this time. The effectiveness of Santopour was 10-12° lower than that of Ftalezin. When it was present in Avtol 10 in a concentration of 0.5%, the congelation temperature was depressed by 38°, an achievement equalled by no other additive. Avtols with an admixture of 0.5% Ftalezin have a congelation temperature of minus 42-44° and can be used in all the northern regions of the USSR.

In Figure 1 is shown the change of the congelation temperature of Avtol 10 purified with sulfuric acid for different concentrations of the additives. Analogous curves were also obtained for the other oils.

The amount of depression of the congelation temperature of an oil depends on the concentration of the additive in the oil. It is expedient not to use the absolute values of depressions, but the effectiveness, which is understood to mean the depression of the congelation temperature of an oil which is attributable to each gram of the additive dissolved in 100 g of oil. The effectiveness of an additive decreases as its concentration in the oil is increased. Formation of a mathematical expression for the law according to which the effectiveness of an

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additive varies with its concentration in oil enabled us to render an opinion concerning the physical and, in particular, the kinetic nature of the additive: moreover, it makes possible a theoretically understandable approach to solving the problem of the selection of additives for oils of different types.

The effectiveness of different additives varies according to an identical law in oils of different types. We examined the character of the functional dependence of effectiveness on concentration. We found that the square root of the effectiveness [Э] is a logarithmic function of the concentration [C].

Proof of the applicability of the equation $Э^{1/2} = K \ln C$ showed that the function acquires a linear character if we plot on the coordinate axes the values of the argument and the corresponding values of the argument's function.

This is illustrated by the two examples shown in Figures 2 and 3. We also obtained analogous dependences in other cases. The graphs reproduced in Figures 2 and 3 show that for each oil there exists a region where the effectiveness of different additives at the same concentration becomes almost the same. For oils possessing a high degree of compatibility with admixtures, for example, Avtol, the effectiveness of different additives is very nearly equal at 1% concentration, while for oils possessing a low degree of compatibility with additives, for example, machine oil, the effectiveness will be the same at a higher concentration, approximately 5-6%. These concentrations at which additives are equally effective can be called critical, since at concentrations higher than these values the order of effectiveness of the additives is reversed. The most highly effective additive becomes the least effective, and vica versa in the series of additives being described. Up to the critical zone, for example, at 0.5% concentration, the effectiveness of the additives drops off in the following order: Ftalezin, Santopour, Naftezin, Paraflow. Beyond the critical zone, whose position depends on the type of oil and usually lies at a concentration of the additives of between 1 and 6%, the effectiveness drops off in the following reverse order: Paraflow, Naftezin, Santopour, Ftalezin.

The more effective an additive is, the sooner it loses its effectiveness in oil. As the concentration is increased, the effectiveness of the additive will be lost for Ftalezin at the lowest concentrations, for Santopour at higher, for Naftezin at still higher, and for Paraflow at the highest concentrations. The region at which effectiveness of additives is lost in oils having a high compatibility with additives (Avtols) lies at higher concentrations than the region at which additives for oils with low compatibility (machine oil) lose their effectiveness.

Parafow, the least effective of the additives described, retains its effectiveness in machine oil S over the whole possible range of concentrations. Ftalezin, the most highly effective additive, loses its effectiveness at a concentration of 3% in the most compatible of the oils studied by us (Avtol 10 purified with sulfuric acid).

Additives prepared on the basis of isoparaffin hydrocarbons of petrolatum were extremely effective.

Conclusions

1. New, highly effective additives were prepared for reducing the congelation temperature of lubricating oils. These additives were found to be more effective than Paraflow and Santopour.

2. We explained the character of the variation of the effectiveness of additives with the change of their concentrations in oil and with the change of the nature of the oil.

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1. Davis, US Patent 1825022, from 14/VII, 1931.
2. Reiff, Badertsher, US Patents 2048465 and 2048466.

Table 1. Constants of Oils Used for Testing of Depressants

Designation of Oil	Sp W d_4^{20}	Engler Viscosity at 50°C	Congelation Temp in °C
Avtol 10 purified with sulfuric acid	0.8955	12.20	-4
Avtol 10 purified with furfurol	0.9092	8.81	-12
Aviation oil MK	0.8945	23.04	-24
Machine oil S	0.9136	6.33	-27

Table 2. Congelation Temperatures in °C of Oils With Admixtures of Paraflow and Naftezin

		Admixture of 0.5±0.02%		Admixture of 1±0.02%	
Oil	Pure Oil	US Paraflow	Naftezin	US Paraflow	Naftezin
Avtol 10 purified with sulfuric acid	-4	-22	-23	-26	-34
Avtol 10 purified with furfurol	-12	-29	-36	-32	-40
Aviation oil MK	-24	-32	-37	-36	-42
Machine oil S	-27	-34	-36	-38	-41

Table 3. Congelation Temperatures in °C of Oils With Admixtures of Santopour and Ftalezin

		Admixture of 0.25±0.01%		Admixture of 0.5±0.02%	
Oil	Pure Oil	US Santopour	Ftalezin	US Santopour	Ftalezin
Avtol 10 purified with sulfuric acid	-4	-24	-34	-30	-42
Avtol 10 purified with furfurol	-12	-32	-40	-36	-44
Aviation oil MK	-24	-35	-39	-39	-44
Machine oil S	-27	-36	-41	-40	-46

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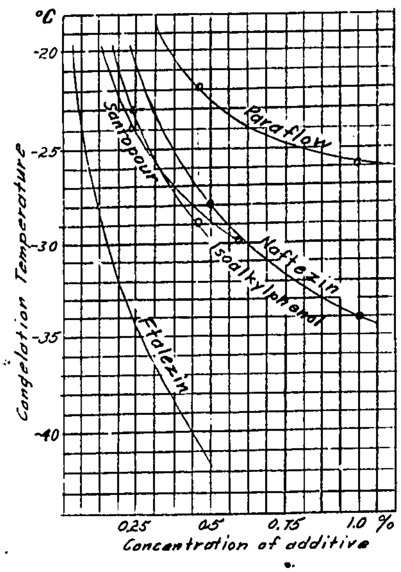

Figure 1. Variation of congelation temperature of Avtol 10 (purified with sulfuric acid) with the concentration of V the additive in the oil.

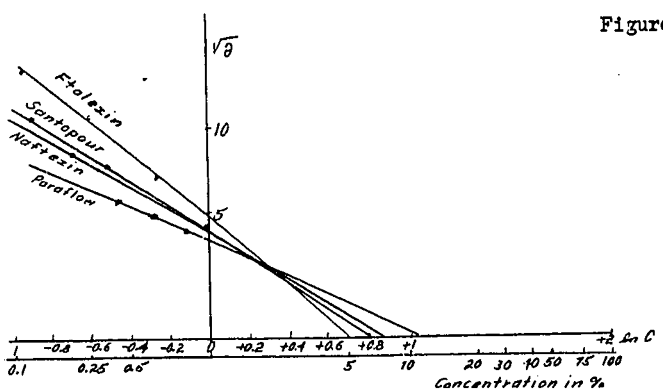

Figure 2. Variation of the effectiveness of additives with their concentration in Avtol 10 purified with furfurol, representing the relationship $\vartheta^{1}/2 = K \ln C$

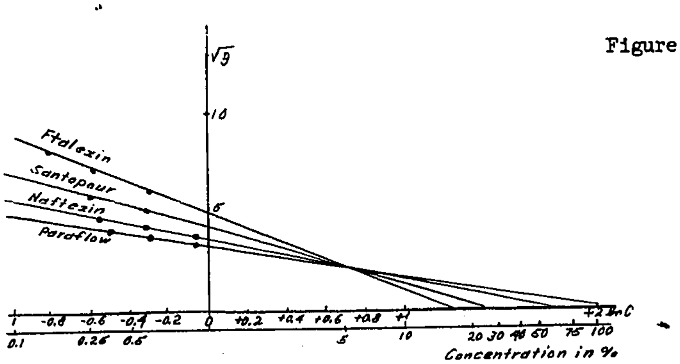

Figure 3. Variation of effectiveness of additives with their concentration in machine oil S, representing the relationship $\vartheta^{1}/2 = K \ln C$

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